**MAHARSHI DAYANAND SARASWATI UNIVERSITY,**

**AJMER**

**Appendix-IV-A**

**Format for outline of proposed research work**

**1.** Name of Scholar (in English) - Anjali Dadheech

(in Hindi) - ***vatyh nk/khp***

2. Title of the Research work -

(in English) - "Studies on Synthesis of Ag and ZnO/Mn Nanocatalyst and its use to Photocatalytic degradation of Textile Dyes."

(in Hindi) - **"flYoj] ftad vkDlkWbM @eSaxuht uSuks mRizsjd dk la'ys"k.k ,oa bldk oL= jatdks ij izdk'k mRizsjdh vi?kVu esa mi;ksx dk v/;;uA"**

3. Location:

a. Institute /Department where the work is to be done -

Department of Chemistry,

M.L.V. Govt. College, Bhilwara, Rajasthan

**4. Introduction, Importance of proposed investigation**

**Introduction :**

At the present time, great efforts are being expended to minimize the quantity and the toxicity of industrial effluents. Considering the inherent toxic nature of industrial effluents and the unavailability of clean technologies the necessity of developing new methodologies for efficient treatment of effluents is evident. In the case of textile industry, the more complex environmental problems associated with the effluents are due to extensive use of carcinogenic or mutagenic dyes which are resistant to microbial degradation. Some dyes are either toxic or can be modified biologically to toxic or carcinogenic compounds. The non biodegradability of textile wastewater is due to their high content of dyestuffs, surfactants and additives[1]. There are no universally useful methods available for treatment of dye wastes, probably because of the complex and varied chemical structures of these compounds. The most popular treatment to eliminate toxic compounds from the waste are flocculation, adsorption and biotreatment[2].

Advanced oxidation processes, which involve participation of hydroxyl radicals are used to degrading toxic organic compounds to CO and OH without the use of chemical oxidants. Photocatalytic treatment of effluents frequently involves the use of U.V. light & aqueous suspension of semiconductor metallic oxides, usually $TiO_2$, SnO and fenton reagent etc[3,4].

However only a small portion (<5%) of solar energy reaching the surface of the earth is UV light, which is probably too little to achieve significant photo degradation rates for the practical application of $TiO_2$/ Visible light[5] system in the treatment of wastewater by this "photocatalytic Oxidation" mechanism.

The type 1 photo-oxidation via electron transfer from a dye stuff absorbed on a semiconductor surface plays an important role in the photographic and solar energy conversion. Organic dyes such as cyanin dyes, squarine dyes, oxazine dyes,

quinine dyes, xanthenes dye and azo dyes have been used widely as photo sensitizers.

Dyes have been used in the textile industry and photochemical applications depending on the chromogenes, chromophores and auxochromes. Dyes exhibit different physical and chemical properties such as water solubility, colour, brightness, fastness and light absorption characteristics. Many dyes pose environmental hazards because there degradation may produce toxic intermediates for example- those dyes containing structures of nitrobenzene, azoheterozole, paradiaminobenzene, stilbene, aminonaphthol, benzidine and quaternary amines have carcinogenic and toxic effects which concerns with increasing awareness of protection of water resources to ensure a safe drinking supply[6].

A powerful and clean oxidizing agent is the UV radiation itself. It has tremendous oxidation potential which is normally enough to interact with the electronic structure of the matter. The degradation of the organic pollutant is normally initiated from an electronic excited state which can undergo homolytic bond fission to form radicals that will react towards final product in a chain reaction with the participation (or not) of molecular oxygen or initiate a process of electron transfer to a ground state oxygen molecule .

$$R \xrightarrow{h\nu} R^*$$

$$R \longrightarrow R'_1 + R'_2 \longrightarrow \text{Products}$$

$$R^* + O_2 \longrightarrow R' + O_2$$

The resulting radical, cation can undergo hydrolysis or mesolytic superoxide radical ion ($O_2$) is known to be capable of degrading aromatic molecules[7].

Semi conductors (such as $TiO_2$, ZnS, $Fe_2O_3$, CdS) can act as sensitizers or light induced redox processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and anti conducting band[8,9,10]. A lot of studies have been reported on the photocatalytic degradation of hazardous organics. Studies in this field found the compounds degraded by photocatalysis using ZnO and $TiO_2$ by various researchers[11,12,13,14,15,16], and using metal deposited on catalyst surface[17]. Degradation studies of thiourea with $H_2O_2$ and fenton[18] reported. Homogeneous, heterogeneous oxidation also studied[19] and also in situ catalytic oxidation reported[20]. $TiO_2$ as a catalyst used for photo catalytic water splitting[21]. Efficiency towards photo catalytic degradation for UV/$TiO_2$, UV/ZnO and photo fenton reagent[22] also reported. Harmful effects of organic dyes in waste water have been a major concern and now a major threat in the environment due to the substantial pollution caused by them. Textile, plastic, medicine and many other industries exhausted large quantity of high content coloured effluents which are generally more toxic and resistant to destruction by conventional methods.

So in the recent years many research works devoted to improve the photo catalytic activity by incorporating with metal particles (Ag, Au, Fe, Cu[23]) to broaden the absorption of the solar radiation by doping reactivate the $TiO_2$ based photo catalyst by treating with heat.

An alternative type of catalyst for photo degradation of organic dyes is nano particles of some transition metals such as Fe, Au, Zn[24], Ag[25], Mo and Ag/ZnO[26]

nanostructures the size, shape, large surface area to volume ratio and mass dependent reactivity has made metal nanoparticles high photocatalytic activities. Now a days nanocatalysts are widely used for the effective removal of dye contaminants.

The focus of the present research work is to apply the accurate principles of green chemistry for the synthesis of Ag and plasmon mediated ZnO/Mn solar active nanocatalyst and its application to photocatalytic degradation of textile dyes.

**Importance of proposed investigation:**

1. The efforts for proposed investigation are helpful to minimize the quantity and the control toxicity of textile industrial waste water.
2. Proposed research work is non toxic, and low cost method will used for the photo degradation of textile dyes.
3. The preparation of photocatalyst material is capable of selective photocatalytic degradation of organic pollutants.
4. Design of more reliable photocatalyst that can be photo activated by UV-visible and solar light both.
5. The examination and the analytical methods of the prediction of useful end products is effective for the transfer of the technical knowledge how to the collaroborative textile industries.
6. The comparison of the results of photo decolourisation efficiencies with solar irradiation and UV irradiation and the examination of the possibilities of a cost effective method that transfer to increase significantly the efficiency of photo degradation of textile dyes.

**Objectives:**

The main objectives of the present study are :-

1. To study green method to the synthesis of silver and plasmon mediated ZnO/Mn nanocatalyst.
2. To study the crystallinity, phase and purity of the synthesized catalyst which is to be determined by X-ray diffraction patterns obtained by XRF of Ag and ZnO/Mn nanocatalyst.
3. To examine the synthesis of Ag and Zno/Mn nanoparticles by using FTIR spectrophotometer.
4. To study the photo degradation of toxic textile dyes primary monitored on methylene blue, methyl orange and malachite green dye and than on other selected dyes by visible light irradiation which is a green chemistry reaction.
5. To determine the removal performance at different experimental conditions i.e. optimum pH, effect of particle size, effect of adsorbent dosage and initial concentration.
6. To do waste minimization through Cleaner & Greener Technology, Recycle/Reuse/Recover.
7. To study the morphology (size and shape of Ag and ZnO/Mn nano catalyst) by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM).
8. To analyze UV-visible spectra analysis for all samples and the absorption maxima using UV-visible spectrophotometer.
9. To study the photocatalytic activity of nanocatalyst on the degradation of dyes (primarly on methylene blue, methyl orange, and malachite green) in laboratory conditions under illumination of UV light in the photoreactor.

**5.Review:**

Vinodgopal, Wynkoop and Kamaat[27] (1996) discussed photosensitized degradation of a textile azo dye, Acid Orange 7, carried out on $TiO_2$ particles using visible light. Mechanistic details of the dye degradation elucidated by using diffuse reflectance absorption and FTIR techniques. The dependence of the dye degradation rate on the surface coverage show the participation of excited dye and $TiO_2$ semiconductor in the surface photochemical process.

Vinodgopal, Bedja and Kamat[28] (1996) investigated nanostructured semiconductor films of $SnO_2$, $TiO_2$ and $SnO_2/TiO_2$ employed for electrochemically assisted photocatalytic degradation of a textile azo dye naphthol blue black (NBB). The degradation rate was significantly higher for $SnO_2/TiO_2$ composite films than $SnO_2$ and $TiO_2$ films alone.

Wu *et al.*[29] (1998) Studied chemical oxygen demand (COD) and proton NMR, UV−vis, and spin trapping EPR spectroscopic evidence presented to demonstrate the inverse photosensitized oxidative transformation of tetraethylated rhodamine (RhB) under visible illumination of aqueous titania dispersions. Intermediates presented after each de-ethylation step remained in a fast dynamic equilibrium between the titania particle surface and the bulk solution.

Stock *et al.* [30] (2000) Studied the merits of combining two advanced oxidation processes, viz. sonolysis and photocatalysis evaluated by investigating the degradation of an azo dye, naphthol blue black (NBB), using a high-frequency ultrasonic generator and UV−photolysis. Sonolysis was effective for inducing

faster degradation of the parent dye, while $TiO_2$ photocatalysis was effective for promoting mineralization.

Manu and Choudhary[31] (2003) demonstrated decolourisation studies of simulated wastewater containing vat dye (C.I. vat blue 1:indigo) and azo dyes (Reactive blue H3R and Reactive red HE 7B).The performance of the bioreactors was evaluated by monitoring oxidation–reduction potential (ORP) in the reactor, colour and chemical oxygen demand (COD) removal. The results indicated the usefulness of semicontinuous reactors for the degradation of recalcitrant compounds like azo and vat dyes.

Anujaneyulu, Chary and Raj[32] (2005) investigated decolourisation of industrial effluents – available methods and emerging technologies.Data on decolourising efficiencies of different causative agents obtained by means of different physical, chemical and biological methods discussed.

Chatterjee and Dasgupta[33] (2005) examined visible light induced photocatalytic degradation of organic pollutants. These methods broadly divided into two main categories. In the first category, the use of $TiO_2$ semiconductor facilitating the photooxidative degradation of organic pollutants presented. In the second category, various ways of degrading organic pollutants without the use of $TiO_2$ semiconductor.

Amuda[34] (2006) investigated two methods of removal of COD and colour from sanitary leachate. The first methd coagulation/flocculation process which involved $FeCl_3$, as conventional coagulant and $Ca(OH)_2$ as base precipitant.The

second method involved integration of fenton reagent to the previous method.The first method reduced chemical oxygen demand by 32% and colour by 62% while the second method reduced chemical oxygen demand by 88% and colour by 98%.

Tayade *et al.*[35] (2007) Investigated photocatalytic degradation of acetophenone, nitrobenzene, methylene blue and malachite green present in aqueous solution using nanocrystalline anatase and rutile $TiO_2$.Concluded that higher photocatalytic activity in anatase $TiO_2$ is due to parameters like band gap, number of hydroxyl groups, surface area and porosity of the catalyst.

Asiltark *et al.*[36] (2009) Studied effect of $Fe^{3+}$ ion doping to $TiO_2$ on the photocatalytic degradation of malachite green dye under UV and visible irradiation using XRD, SEM and UV/VIS/NMR techniques, synthesized nano particles were of nano scale. Rate kinetics followed the pseudo first order reaction.

Wang *et al.*[37] (2008) Investigated operational parameters photocatalytic degradation of C.I. Basic violet 10 using $TiO_2$ catalyst supported by Y zeolite. . The physical and chemical states of Zeolites - supported $TiO_2$ evaluated via powder X-ray diffraction (XRD), fourier transform infrared (FTIR) and nitrogen adsorption- desorption isotherms. The photocatalytic reaction followed first order kinetics for all catalysts.

Tiwari, Behari and Sen[38] (2008) discussed application of nanoparticles in waste water. Basically four classes of nano scale materials evaluated as functional materials for water purification are - 1) metal containing nanoparticles, 2) carbonaceous nano materials, 3) zeolites, 4) dendrimers. Nano materials revealed good result than other techniques because of its high surface area.

Gaya and Abdullah[39] (2008) reviewed fundamental progress and problems of heterogeneous photocatalytic degradation of organic contaminants over

Titanium dioxide. $TiO_2$ photocatalyst remains a viable alternative for the degradation of persistent organic contaminants in both air and water.

Akpan and Hameed[40] (2009) reviewed the effects of operational parameters affecting the photocatalytic degradation of dyes using $TiO_2$ based photo catalysts. . Oxidising agents, calcination temperature and catalyst loading are found to exert their individual influence on the photocatalytic degradation of any dye.

Alexandre *et al.*[41] (2009) Investigated photocatalytic decolouration of malachite green dye by $TiO_2$ application of $TiO_2$ nanotubes. Synthesis of nanotubes was carried by hydrothermal system and characterized by using techniques like SEM,FTIR, FT-Raman and surface area analyzer.

Rauf and Ashraf [42] (2009) studied fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. Using $TiO_2$ as a catalyst and azo dye. techniques- UV-vis spectrophotometry, MS, HPLC, ion chromatography, capillary electrophoresis, radiometry, photocatalytic reactor. Cationic dye undergoes faster degradation than the anionic dyes.

Farha[43] (2010) Demonstrated photocatalytic degradation of acid orange 10 and acid red 114 dyes in waste water on nanometer sized $TiO_2$. The rates of disappearance of two azo dyes were monitored spctrophtometrically at the visible maximum absorption wavelengths.The rate of reaction follow pseudofirst order kinetics.The photocatalytic degradation rate depends on dye structure, dye concentration, $TiO_2$ concentration and pH of the medium.

Rauf *et al.*[44] (2010) Studied photo induced degradation of methylene Blue (MB) dye in the presence of Ti, Cr with UV-Vis absorption. Photocatalytic degradation of the dye followed the pseudo-second-order-kinetics. Degradation

product analysis was done using the LC-UV/Vis-MS technique and the results shown that the dye degradation was initiated by demethylation of the molecule.

Gupta *et al.*[45] (2011) Demonstrated the removal of the dye tartrazine by photodegradation using titanium dioxide surface as photocatalyst under UV light. The process was studied out at different pH, catalyst dose, dye concentration and effects of the electron acceptor $H_2O_2$. It was found that under the influence of $TiO_2$ as catalyst, the coloured solution of the dye became colourless and the process followed a pseudo first order kinetics.

Rauf, Meetani and Hisaindee [46] (2011) discussed an overview on the photo catalytic degradation of azo dyes in the presence of $TiO_2$ doped with transition metals using technologies - UV vis spectrophotometry, LC/MS, HPLC ion chromatography, capillary electrophoresis, FTIR & NMR & photochemical reactor. Such dopants reduce the recombination of $e^-$ cb and $h^+$ vb and decrease the band gap or create intra gap states which results in more light absorption.

Saggioro *et al.*[47] (2011) Studied photocatalytic degradation of two commercial textile azo dyes namely C. I. Reactive Black 5 and C.I. reactive red 239. $TiO_2$ Degussa was used as catalyst and photo degradation was carried out in aqueous solution under artificial irradiation with a mercury vapour lamp. After five cycles of $TiO_2$ reuse the rate of colour lost was still 77% of the initial rate.

Surana *et al.* [48] (2011) Studied removal efficiency of azo dye reactive red 198 (RR 198) from aqueous solution using the photo- fenton process. The photo catalytic degradation of RR 198 was observed at 520 mm. Kinetic studies revealed that photo catalytic bleaching of Reactive Red 198 followed a first order kinetics.

Daghrir *et al.*[49] (2012) Studied photoelectrocatalytic technologies.These techniques have particular attension due to their effectiveness in the photo degradation of refractory organic and microbial pollutants present in waste water.$TiO_2$ due to its excellent chemical and physical properties.

Dwivedi and Pande[50] (2012) studied photo chemical degradation of Halogenated compounds. The progress of the photochemical reaction and the rate of the reaction followed by techniques such as Fluorimetry, UV-Vis spectrophotometry, bras chromatography. Photochemical degradation is a very useful and efficient technique to solve many environmental problems.

Eskizeybek *et al.*[51] (2012) Studied preparation of the polyaniline / ZnO nano composite and its photocatalytic activity for degradation of Methylene Blue and malachite green dyes under UV and natural sun lights irradiation. PANI/ ZnO nano composite photocatalysts (0.4g/L) degraded both of dye solution (MB or MG) with 99% efficiency after 5 h of irradiation under natural sunlight.

Gaikwad *et al.*[52] (2012) Studied a green chemistry approach for synthesis of $CaTiO_3$ Photo catalysts : its effects on degradation of methylene blue, photo toxicity and microbial study The structural and microstructural properties of $CaTiO_3$ material was characterized by various analytical practices like FT-IR, UV-DRS, XRD, SEM, & BET.

Giwa *et al.* [53] (2012) Studied solar photocatalytic degradation of reactive yellow 81 and reactive violet 1 in aqueous solution containing semiconductor Oxides with $TiO_2$ (Degussa) as photo catalyst. Chemical Oxygen demand and UV-Vis- spectrophotometer were used to study the mineralization and degradation of the dyes respectively.

Jafari *et al.*[54] (2012) Studied degradation of a textile reactive azo dye by a combined biological photocatalytic process . A two step treatment process namely biological treatment by yeast followed by photo catalytic degradation was also assessed.

Mehra and Sharma[55] (2012) discussed photocatalytic degradation of methyl orange and methylene blue by heterogeneous photocatalytic process using $TiO_2$ as semiconductor catalyst. The initial rate of photo decolourisation increased with increase in catalyst dose up to an optimum loading after that it did not show any effect.

Nihalani *et al.*[56] (2012) Studied photocatalytic water treatment by an ecofriendly process using a new semiconductor Barium Strontium titanate ($Ba_3$ TiO. $SrO_3$ TiO) in degradation of malachite green and crystal violet in aqueous suspension. It was observed on kinetic parameters that the process followed pseudofirst order rate law.

Cheng *et al.*[57] (2013) Studied Au- nano particle loaded graphitic carbon nitride nanosheets : Green photocatalytic synthesis and application toward the degradation of organic pollutants. The nano hybrids shown superior photocatalitic activities for the decomposition of methyl orange.

Harikumar *et al.*[58] (2013) Studied photocatalytic degradation of textile dyes by hydrogel supported, titanium dioxide nanoparticles using UV radiations & scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) & photocatalytic reactor. Calcium alginate can be used as green support for immobilizing $TiO_2$ nanoparticles.

Xuxiang *et al.*[59] (2013) Studied destruction of cyanobacterial toxics. . pseudofirst order reaction rate constants of increased linearly with increasing initial oxidant concentrations.

Jadhav *et al.*[60] (2013) Investigated degradation of dyes using high temperature stable anatase nanosphere $TiO_2$ photocatalyst it was prepared by $TiCl_3$ precursor.Prepared $TiO_2$ was characterized by XRD, UV, SEM, and TEM for their structural, optical, and morphological study.Crystalline anatase form of $TiO_2$ at annealing temperature 400 $^0$C show high thermal stability to retain the anatase form.

Jiang *et al.*[61] (2013) Demonstrated optimization of photocatalytic performance of $TiO_2$ coated glass microspheres using response surface methodology and the application for degradation of dimethylphthalate.

Mirada *et al.*[62] (2013) Investigated improved photocatalytic activity of g-$C_3N_4$/$TiO_2$ composites prepared by a simple impregnation method. Enhanced photoactivites obtained for composites systems. The effective charge carrier separation proposed as the responsible for such improved activites.

Sima and Hasal[63] (2013) Studied photocatalytic degradation of textile dyes and focused on development of a method of $TiO_2$ immobilization methylene blue as a model dye. Application of poly vinyl alcohol revealed to be more convenient than application of the polyacrylamide as the observed degradation rate was much faster with the PVA. High light intensity made the dye degradation substantially faster.

Meena and Meena[64] (2014) investigated treatment of textile industrial waste water of Bhilwara by using nano technology.

Ganaprakasam, Sivakumar and Thirumarimurugan[65] (2015) reviewed influencing parameters in the photo catalytic degradation of organic effluent via nano metal oxide catalyst.

Janani, Henry and Edwine[66] (2015) investigated Optimization of photocatalytic degradation of reactive blue dye using ZnO catalyst. Dye solution (10 mg/l) was used to contact with the zinc oxide catalyst under UV light. The optimum conditions observed for degradation were; catalyst dose of 5.0 g/l, a neutral pH of solution at 7.0, and contact time of 180 minutes (3.0 hours).

Sowbhagya and Ananda [67] (2015) studied synthesis and characterization of Mo-doped ZnO nano particles by electrochemical method and kinetics of methyl violet dye and antibacterial activity of nanoparticles.Synthesized nanoparticles characterized by UV-Vis spectroscopy, IR spectroscopy, SEM and X-ray diffraction techniques.The degradation efficiency of Mo- doped ZnO was found to be 94%.

Abbas *et al.*[68] (2016) Investigated synthesis of nano-sized $SrTiO_3$ catalyst and its doping with Ga and Fe. Prepared by route precursor method using TEM,XPS, and UV-visible spectrophotometer. The effect of doping on the structural properties and the photocatalytic activity was studied. Enhancement in the photocatalytic activity observed than the bared catalyst.

Ma *et al*.[69] (2016) Studied to improve catalytic efficiency and reduce the amount of silver consumption, nanophase of silver phosphate was dispersed on an exfoliated bentonite (EB) to prepare the EB–$Ag_3PO_4$ photocatalyst. The ssynthesized samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Ultraviolet–vis (UV–vis) diffuse reflectance spectroscopy (DRS) and the

Brunauer, Emmett, and Teller (BET) method. The results of improved photoactivity were mainly attributed to the electrostatic interaction.

Pamecha, Mehta and Kabra[70] (2016) studied efficiency of $CeFeO_3$ as photocatalyst for degradation of coralene dark red 2B (Disperse red 167). Photocatalytic bleaching of coralene dark red 2B was observed spectrophotometrically observed.

Pol *et al.*[71] (2016) Investigated Ni-, Pt- and (Ni/Pt)-doped $TiO_2$ nano photocatalysts: A smart approach for sustainable degradation of rhodamine B dye. Ni and Pt NPs hosted by the $TiO_2$ framework in the form of small nano particles. Photo degradation of RhB in aqueous medium had been investigated under UV–vis light. The presence of 1 wt% Ni, Pt NPs significantly enhanced the photocatalytic activity.

## 6. Research gaps identified in the proposed field of investigation:

Modern textile dyes are characterized by strong structural and colour stability due to their high degree of aromaticity and extensively used in many fields and their unintended release into the environment poses potential risk to human health and ecological systems .Thus effective removal of toxic textile dyes from waste water is highly important.

A lot of research have been reported on the photocatalytic degradation of refractory organics. As the literature survey presented the advanced oxidation processes generally involve the $UV/H_2O_2$, $UV/O_3$, UV/ fenton reagent, for the oxidative degradation of contaminants. Semiconductor photocatalysis is a newly developed advanced oxidation process, semiconductor such as $TiO_2$, $Fe_2O_3$, CdS

and ZnS. Among the semiconductor materials suitable for photocatalytic reactions $TiO_2$ and ZnO received much attension due to their easy availability, non toxicity, thermal and chemical stability and its application towards photodegradation. It has been reported on the basis of literature study that ZnO is more efficient than $TiO_2$ for photodegradation of textile dyes. Additionally higher quantum efficiency is an added advantage for ZnO over $TiO_2$ as a photocatalyst for degradation of textile dyes.

Since 46% of solar energy consist of visible light, it is more economical to use visible light than UV light in large scale operations. To use visible light ZnO has several drawbacks including the surface area or big particles size and an unsuitable band gape energy. Recently there has been much attension focused on modifying ZnO by doping with transition metals. It was observed that Doping with 3d metals reduced Eg of semiconductors by forming interband –gap localized levels. Additionally reported results of Mn doped ZnO being applied as a photo catalyst are quite different.

Nanotechnology and the green chemistry is the new emerging trend in modern era. In recent years noble metal nano particles have been the subjects of focused researches due to their unique electronic, optical, mechanical magnetic and chemical properties that are significantly different from those of bulk materials. These special and unique properties could be attributed to their small sizes and large specific surface area. For these reasons metallic nano particles have found uses in many application s in many different fields as catalysis, electronics, and photonics.

Thus the present investigation involve the synthesis of silver(Ag) nano particles and Mn doped ZnO (ZnO/Mn) nano catalyst and its application towards the photo catalytic degradation of textile dyes will proposed.

**7.Hypothesis of research work:**

1. Assuming that when textile dyes subjected to silver and ZnO/Mn nano catalyst the effect will be on the degradation of organic dyes that there may be enhancement in the rate of degradation with respect to the concentration of the catalysts.
2. Assuming that by increasing the concentration of synthesized silver and manganese doped zinc oxide nano catalyst dosages the degradation rate will be affected.
3. Use of synthesized nano catalysts as Ag and ZnO/Mn assumed to be a green synthetic strategy adopted for nanoparticles synthesis by using ecofriendly and renewable molecules to get rid of hazards arising out of the use of chemical reducing agents and organic solvents.
4. Assuming that this colloid based nanotechnology development will be helpful to control the size, shape, uniformality and functionality.
5. Assuming that the present synthesis of Ag and ZnO/Mn nano catalyst will be helpful to reduced synthesis of nano particles and their reduction properties.
6. This new green chemistry approach by using the Ag and ZnO/Mn nano catalyst and degradation of toxic textile dyes will be effective and economic.

**8. Research methodology:**

1. **Dyes**:- Methylene blue, Basic green 4, methyl violet, methyl green, methyl orange , acid black 26, acid blue 9, basic blue 41, basic violet 16, disperse blue79, disperse red 60, disperse yellow211, reactive blue220, vat orange 2.

2. **Chemicals for catalyst synthesis**:- 0.001M silver nitrate solution, poly vinyl alcohol,0.001M of sodium borahydride solution.

   Zinc acetate, Ethanol, Sodium hydroxide, Manganese acetate.

3. **Techniques**:-

   -UV visible spectrophotometer

   -FTIR spectrophotometer

   -Scanning electron microscope

   -Fluorescent spectrophotometer

   -XRF

   -TEM

4. **Methods**:-

   Chemical reduction method[72]

   Precipitation method[73]

5. **Experimental**:-

   Synthesis of catalyst, Characterization of catalyst.

6. Operational parameters affecting the photo catalytic degradation of dyes:-

Determine the removal performance at different experimental conditions i.e. optimum pH, effect of particle size, effect of adsorbent dosage and initial concentration.

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**Signature of the candidate with date**

Outline approved

**Name and signature of Supervisor with date & seal**

**APPENDIX- VI**

MAHARSHI DAYANAND SARSWATI UNIVERSITY,AJMER

**Certificate By Supervisor**

**Certified that:**

1. I am willing to guide the research work of **Anjali Dadheech** on the above subject if he/she is registered for Ph.D.
2. To the best of my knowledge, the subject selected has not been studied and is not being studied so far in any university.
3. The subject is of sufficient scope to keep the candidate engaged for two years.
4. The subject will lead to a valuable contribution. I have seen and approved the outline of proposed research work submitted by the candidate.

5. I have 0 Research candidates registered under my supervision and the serial number of this candidate whose application is being forwarded for registration is 01.
6. The candidate is not in a close relation (the term of close relation is defined in the examination ordinance of the University).

Signature of the Supervisor

with date

Certified that the above facilities will be extended to **Anjali Dadheech** for research work if he/she is registered for Ph.D.

Signature of the Principal with date

Signature of the Head Dept.with date